

(12)

EUROPEAN PATENT APPLICATION

(21) Application number: 82304596.8

(51) Int. Cl.³: **A 61 K 7/13**

(22) Date of filing: 01.09.82

(30) Priority: 03.09.81 GB 8126700

(43) Date of publication of application:
16.03.83 Bulletin 83/11

(84) Designated Contracting States:
AT BE CH DE FR GB IT LI NL SE

(71) Applicant: **UNILEVER PLC**
Unilever House Blackfriars P O Box 68
London EC4P 4BQ(GB)

(84) Designated Contracting States:
GB

(71) Applicant: **UNILEVER NV**
Burgemeester s'Jacobplein 1 P.O. Box 760
NL-3000 DK Rotterdam(NL)

(84) Designated Contracting States:
BE CH DE FR IT LI NL SE AT

(72) Inventor: **Pike, Barry Graham**
April Cottage Pipers Lane
Lower Heswall Wirral Merseyside(GB)

(74) Representative: **Tonge, Robert James et al,**
Unilever PLC, Patent Division PO Box 31 Salisbury
Square House Salisbury Square
London EC4P 4AN(GB)

(84) Hair dye composition.

(87) A composition for use in the dyeing of keratinous fibres, particularly human hair, in order to produce a black colour, comprises an aqueous, substantially oxygen-free solution of the dye precursors 2-methoxy-p-phenylenediamine and 2,4-diaminophenol, the composition having a pH value of from 6 to 12. The molar concentration of one dye precursor to the other is preferably from 1:10 to 10:1, and together they form from 0.25 to 15% by weight of the composition. Optionally, the composition can also contain a detergent and/or a thickening agent.

EP 0 074 243 A1

HAIR DYE COMPOSITION

The invention relates to compositions for dyeing keratinous fibres, and more particularly to hair colourants.

For almost a century, p-phenylenediamine and
5 p-toluylenediamine have both been recognised as primary intermediates in the dyeing of the hair. When mixed with hydrogen peroxide and applied to the hair, a proportion of the mixture migrates into the hair shaft and there reacts to form a permanent colour. However, this procedure
10 suffers from three disadvantages: firstly, the need to keep the intermediate and oxidising agent separate until immediately prior to use, secondly, the need to mix the intermediate and oxidising agent properly immediately prior to use and, thirdly, the risk that excess oxidising agent
15 might cause damage to the hair if too little intermediate is employed, or if mixing of intermediate and oxidising agent is incomplete.

Certain substituted p-ph nylenediamines, notably 2-methoxy-p-phenylenediamine, also known as

2,5-diaminoanisole, have been shown, for example in British Patent Specification No 1,012,793, to be useful as dye intermediates in the dyeing of hair or wool, particularly in the presence of hydrogen peroxide, when a grey colour
5 was obtained.

Certain other substituted benzene compounds such as 2,4-diaminophenol have also been known for many years as dye intermediates in the dyeing of hair by the formation of a permanent colour within the hair shaft after reaction
10 with atmospheric oxygen. This principle is well established and is discussed, for example in Venkataraman K, (1971), "The Chemistry of Synthetic Dyes", Volume 5 at page 475 et seq., and particularly on page 497, where it is reported that a red-brown colour was obtained with
15 2,4-diaminophenol.

Inspite of the considerable amount of research which has been conducted in this field, it has hitherto not been possible to provide a system based on an autoxidation reaction which will impart to living human hair, within a
20 short contact time, a black or nearly black colour.

We have now, however, discovered that a mixture of 2-methoxy-p-phenylenediamine and 2,4-diaminophenol can successfully be employed as dye precursors to impart a black colour to the hair, in the absence of a peroxide
25 commonly used as an oxidising agent in the dyeing of hair.

Furthermore, we have shown that the addition of either p-phenylenediamine or p-toluylenediamine to a mixture of 2-methoxy-p-phenylenediamine and 2,4-diaminophenol does not further enhance the dyeing operation nor do they influence
30 the intenseness of the black colour obtained.

Accordingly, the invention provides a composition for use in the dyeing of keratinous fibres to produce a black colour, which comprises an aqueous, substantially oxygen-free solution of 2-methoxy-p-phenylenediamine and
35 2,4-diaminophenol, the composition having a pH value of from 6 to 12.

It should be explained that "keratinous fibres" are fibres having the basis of the protein keratin. Although animal hair such as wool is an example of "keratinous fibres" and can accordingly be dyed using compositions of the invention, the invention herein is described and illustrated for convenience in terms of human hair which is a further example of "keratinous fibres". The invention is furthermore applicable both to "keratinous fibres", such as hair on the human head, or to wigs and hair pieces made from human hair.

The 2-methoxy-p-phenylenediamine and the 2,4-diaminophenol, hereinafter referred to as "the dye precursors", together form from 0.25 to 15%, preferably from 1 to 10% by weight of the composition.

If less than 0.25% by weight of the dye precursor mixture is employed, then the composition is unlikely to dye hair a black colour, whereas if more than 15% by weight of the dye precursor mixture is employed, it is unlikely that the depth of the black colour produced in the hair will be further increased beyond that obtained when up to 15% by weight of the precursors is employed.

The minimum concentration of each dye precursor to be employed will depend on the mole ratio of each, and on the total concentration of both dye precursors in the composition.

The molar ratio of 2-methoxy-p-phenylenediamine to 2,4-diaminophenol in the composition is accordingly generally from 1:10 to 10:1, the preferred molar ratios being from 1:5 to 3:1, ideally 1:3 to 1:1.

If the dye precursors are employed at concentrations whose molar ratio are outside of the range 1:10 to 10:1, it is unlikely that a good black colour will be achieved.

The concentration of each dye precursors in the composition is generally from 0.1 to 14.9%, preferably from 0.5 to 10% and most preferably from 1 to 8% by weight.

The 2-methoxy-p-phenylenediamine is conveniently

employed in the form of its sulphate-monohydrate weight : 254), as supplied for example by Aldrich Chemicals Limited. The 2,4-diaminophenol is conveniently employed in the form of its dihydrochloride salt (molecular weight :
5 197), as supplied for example by Koch Light Limited. When the pH of the composition is adjusted to a value from 6 to 12, these salts will give rise to the respective dye precursor bases.

The compositions according to the invention should be
10 substantially free from oxygen in order to prevent oxidation of the dye precursors taking place before application to the hair. It is accordingly apparent that if either of the dye precursors is exposed to oxygen, then some oxidation is likely to occur, and the hair to which
15 the composition is subsequently applied may not acquire a black colour. 2,4-diaminophenol is particularly prone to autoxidation in this way.

It is therefore necessary to ensure that all or substantially all oxygen is removed from the composition
20 and that access of oxygen is prevented until such a time as the composition is required for dyeing hair.

The ingredients of the composition and the composition itself can be purged of oxygen by preparing and packing the composition in the presence of an inert gas such as for
25 example nitrogen, carbon dioxide or a liquefiable gaseous propellant.

As an alternative, or additional to the use of an inert gas, the composition can contain an antioxidant to scavenge any oxygen that may come into contact with the dye
30 precursors, either during manufacture of the composition or during storage prior to use.

When an antioxidant is employed, suitable antioxidants include, for example, ascorbic acid, sodium metabisulphite and sodium dithionite, or mixtures thereof, which should be

employed in the composition in an amount sufficient to scavenge dissolved oxygen or gaseous oxygen enclosed within the headspace above the composition, while the composition is held in a closed container. Such antioxidants or
5 mixtures thereof can usually be employed in the composition at a concentration of from 0.01 to 2%, preferably from 0.1 to 1% by weight of the composition.

It should be explained that where reliance is placed on the use as an antioxidant as an oxygen scavenger,
10 compositions containing less than 0.01% by weight of antioxidant can contain oxygen that may not be fully scavenged by such a low level of antioxidant, whereas compositions containing more than 2% by weight of
15 antioxidant can have their effectiveness diminished when applied to hair, due to interference with the autoxidation reaction on contact with atmospheric oxygen, on which the production of a black colour relies.

The compositions according to the invention can optionally also contain detergent, although care should be
20 exercised in the choice and/or quantity of detergent employed, as some tend to reduce the intensity of the black colour of the dyed hair, or result in the development of colours other than black.

Suitable detergents for use in the process of the
25 invention can be selected from anionic, non-ionic, amphoteric, zwitterionic and cationic detergents or mixtures of detergents from two or more of these classes detergents.

Examples of anionic detergents include alkyl benzene
30 sulphonates, such as sodium alkyl benzene sulphonates and sodium alkyl naphthalene sulphonates; alkyl sulphates, particularly those having from 12 to 18 carbon atoms in molecule, such as sodium lauryl sulphate and
triethanolamine sulphate; alkyl benzene polyoxyethylene
35 sulphonates, particularly those wherein the alkyl radical has from 8 to 12 carbon atoms; sulphat d monoglycerides,

such as lauric monoglyceride sodium sulphate, lauric monoglyceride ammonium sulphate and sulphated cocomonoglyceride ammonium salt; alcohol ether sulphates; sarcosines, such as lauroyl sarcosine and cocoyl sarcosine; 5 and sulphosuccinates, such as the dioctyl esters of the salts of sulphosuccinic acid.

Examples of cationic detergents include distearyl dimethyl ammonium chloride, dilauryl dimethyl ammonium chloride diisobutylphenoxyethoxyethyl dimethyl benzyl 10 ammonium chloride, cetyl trimethyl ammonium bromide, N-cetyl pyridinium bromide and benzethonium chloride.

Examples of amphoteric detergents include N-alkyl β -imino dipropionates, N-alkyl β -amino propionates and the basic quaternary ammonium compounds derived from 2-alkyl- 15 substituted imidazoline such as hydroxyethyl carboxymethyl alkyl imidazolinium hydroxide (MIRANOL), especially the lauric, myristic or stearic derivatives.

Examples of nonionic detergents include condensates of ethylene oxide with hydrophobic bases formed by condensing 20 propylene oxide with propylene glycol (PLURONICS), nonyl phenoxypoly(ethyleneoxy)ethanol (IGEPAL), and polyoxyethylene(20)sorbitan monooleate (TWEEN 80).

Suitable detergents for use in the process of the invention can also comprise soaps which are water soluble 25 salts of higher fatty acids and include alkali metal soaps such as sodium, potassium, ammonium and alkanol ammonium salts of straight chain saturated or unsaturated fatty acids containing from 8 to 24 carbon atoms, preferably from 10 to 20 carbon atoms. Preferred soaps include potassium, 30 monoethanolamine, diethanolamine and triethanolamine soaps of C_{12} to C_{14} fatty acids, particularly of coconut fatty acids.

It has however been shown that when a detergent is to be incorporated into compositions of the invention, 35 the preferred anionic detergent is one chosen from

Sodium lauryl ether sulphate (2EO) (such as EMPICOL ESB 3S) and

Sodium lauryl ether sulphate (3EO) (such as GENAPOL ZRO).

- 5 When a nonionic detergent is employed, it is preferably mixed with an anionic detergent in order to increase foam volume when the composition is applied to the hair, without reducing the intensity of the black colour produced. Examples of preferred nonionic detergents
- 10 are polyoxyethylene lauryl alcohol:23EO (such as BRIJ 35) and oleic diethanolamide (such as MARLAMIDE D 1885).

The preferred detergent mixture comprises sodium lauryl ether sulphate:2EO with either of the above-named nonionic detergents.

- 15 The quantity of detergent when employed in the composition, will depend on which detergent is chosen and whether a mixture of detergent is employed. Whereas the use of a detergent assists application of the composition to the hair, in that a foam is produced which enables the
- 20 user more readily to distribute the composition evenly onto and thoroughly into the hair, care must be exercised that the quantity of detergent is not so excessive that a black hair colour does not result.

- It is but a simple task to establish a suitable
- 25 quantity of a detergent for this purpose by experimental application of a series of compositions containing differing amounts of detergent to switches of blond hair, and then selecting that composition which produces the pleasing black colour.

- 30 However, by way of example with reference to the preferred anionic and nonionic detergents referred to hereinbefore, the quantity of detergent that can be employed in compositions according to the invention is 1 to 15%, preferably from 5 to 10% by weight of the
- 35 composition, expressed in terms of active detergent.

If less than 1% by weight of any of the preferred

anionic or nonionic detergents is employed, then it is unlikely that the consumer, when applying the composition to the hair, will obtain a significant lather from which the advantages of employing a detergent in the composition can be derived. If more than 15% by weight of any of the preferred anionic or nonionic detergents is employed, then application of the composition to the hair may yield an excessive volume of foam and may result in the development of a hair colour which is not a true black.

10 Ideally, the composition should contain a mixture of the preferred anionic and nonionic detergents at an active detergent ratio of 1:3.

The composition according to the invention can also optionally contain a thickening agent to enable it to be more easily dispensed from a container in a controlled manner, and more readily applied to the hair without, for example, running off the scalp.

Suitable thickening agents include:
carboxyvinyl polymers such as CARBOPOL* 940 and
20 CARBOPOL 941, and
polyethyleneglycol distearate.

Thickening agents such as these can be employed at a concentration of from 0.1 to 2%, depending on the choice of thickening agent. The Carbopols can, for example, be
25 employed at a concentration of up to about 1% and the polyethyleneglycol derivative up to about 2% by weight.

It is also possible to include in compositions according to the invention other ingredients such as conditioners, polymers, preservatives and perfumes, and
30 other ingredients such as are conventionally employed in products intended for the treatment of hair.

The invention also relates to a process for preparing a composition for use in the dyeing of keratinous fibres to produce a black colour, which process comprises

35 * trade mark

the steps of:

- (i) dissolving in oxygen-free water the dye precursors 2-methoxy-p-phenylene diamine and 2,4-diaminophenol, the composition having a pH value of from 6 to 12; and
- (ii) packaging the composition in a closed container in the substantial absence of oxygen.

The pH of the composition so prepared may be adjusted to the desired value of 6 to 12, preferably 7 to 10, by addition of an alkali such as sodium hydroxide or ammonia, or by employing a suitable buffer.

According to a preferred process, the dye precursors are dissolved in an aqueous solution of an antioxidant so as to establish oxygen-free conditions, care being exercised to exclude oxygen, for example by purging with an inert gas.

Optionally, polar organic solvents, such as isopropyl alcohol, may also be added to aid solution of the dye precursors.

The composition should be stored prior to use in a closed container from which it can be readily dispensed when required for application to the hair. The container or dispenser should preferably be one which is airtight or will at least prevent the ingress of atmospheric oxygen sufficient to cause the dye precursors to oxidise prematurely.

Suitable containers include plastic sachets, capped jars or tubes, pump spray operated applicators or pressurised aerosol devices in which liquefiable gaseous propellant can maintain a substantially oxygen-free headspace. The chosen design of the container, dispenser or applicator will depend partly on whether single or multiple dose application is intended, and partly on the means selected for ensuring that the composition is stored in a substantially oxygen-free state.

The preferred closed container is designed to provide

a single dose or so-called one pack product, the contents of which are sufficient to dye one head of hair.

The invention also provides a method for dyeing keratinous fibres which comprises applying to the
5 keratinous fibres a composition comprising a substantially oxygen-free solution of 2-methoxy-p-phenylenediamine and 2,4-diaminophenol, and allowing these dye precursors to oxidise in the presence of atmospheric oxygen.

When hair is to be dyed with compositions according to
10 the invention, it is optionally first washed and then a proportion of the substantially oxygen-free solution containing the dye intermediates is applied to damp but not wet hair, to avoid over dilution of the dye precursors, and thoroughly rubbed in. By way of example, for a normal head
15 of hair (about 70g in weight) about 20 ml of an aqueous solution containing 0.4M of both the dye precursors is applied to the damp hair. Both the duration and temperature of application to the hair will affect the final result obtained. In general, the longer the time and
20 the higher the temperature of contact, the more intense is the black colour of the dyed hair which finally results, but 10 to 30 minutes at room temperature (20° to 25°C) is usually sufficient for the development of a desirably intense black colour. Preferably, dyeing to a black colour
25 is achieved without employing hydrogen peroxide as is conventional in a two-pack hair dye treatment.

It is also possible to apply repeatedly a dilute solution of the mixture of dye precursors in order to darken light or grey hair gradually until a desirably dark
30 or black colour is obtained. As an example, an aqueous substantially oxygen-free solution of 2-methoxy-p-phenylenediamine and 2,4-diaminophenol, each at a concentration of from 1 to 2% by weight can be applied to grey hair once or twice a day for about one week in order
35 to obtain gradual darkening until a near black is obtained.

Usually, 7 to 8 successive applications are sufficient to develop a good black colour to the hair.

Compositions according to the invention are particularly of value in the dyeing of human hair either
5 attached to the head or in the form of a wig, hairpiece or switch. The compositions can however also be employed in the dyeing of natural keratinous fibres such as wool or silk or of synthetic keratinous fibres.

The invention is illustrated by the following Examples
10 of "one-pack" compositions according to the invention containing both 2-methoxy-p-phenylenediamine (MPPD) and 2,4-diaminophenol (DAP).

Example 1

In this example a solution of both dye intermediates
15 in the form of their respective salts was prepared in buffer and the solution stored under nitrogen to provide oxygen-free conditions.

Preparation of buffer

Sodium dihydrogen orthophosphate, 13.6g was dissolved
20 in water, 500 ml, and isopropyl alcohol, 150 ml, was added and the solution made up to 1 litre after adjustment of the pH with sodium hydroxide to 8.0.

Preparation of solution of dye intermediates

76.2g MPPD (as the sulphate monohydrate salt) together
25 with 19.7g DAP (as the dihydrochloride salt) were dissolved in 1 litre of the buffer containing antioxidant to provide a concentration of 0.3M with respect to the MPPD and 0.1M with respect to the DAP.

This mixed solution was prepared under nitrogen and
30 stored in the absence of oxygen until required for use.

Dyeing of hair

A switch of Italian "Blue String" virgin blond hair
(about 1g) was thoroughly wetted with tap water, excess
water removed by blotting with filter paper and immersed in
35 the oxygen-free solution containing the dye precursors in a 5 cm dish open to the atmosphere.

The switch was turned and agitated frequently with a glass rod during dyeing. After immersion for 20 minutes in the dye solution, the hair switch was rinsed and dried.

The switch of hair had a black colour.

- 5 In control experiments in which first the MPPD was omitted, and then secondly the DAP was omitted, similar switches of blond hair were dyed dark brown and pale blue/black respectively.

Example 2

- 10 This example illustrates the inclusion of detergents in compositions according to the invention.

The following formulation was prepared as a "one-pack" product.

<u>Ingredients</u>		<u>% w/w</u>
15	Sodium lauryl ether sulphate (2EO) (EMPICOL ESB 3S : 25% AD)	10.0
<u>Thickener</u>		
	Carboxyvinyl polymer (CARBOPOL 940)	1.0
20	<u>Dye intermediates</u>	
	2-methoxy-p-phenylenediamine: sulphate monohydrate salt (MPPD)	7.62
	2,4-diaminophenol: dihydrochloride salt (DAP)	1.97
25	<u>Solvent for MPPD</u>	
	Isopropanol	2.0
	<u>Antioxidant</u>	
	Sodium metabisulphite	0.5
	<u>pH adjustant to pH 8.5</u>	
30	Ammonium solution	q.s.
	Water	100

The concentration of MPPD can also be expressed as 0.3M and that of DAP as 0.1M.

- 35 The above "one pack" product was successfully stored for four months in the absence of oxygen, without deterioration or loss of viscosity, at temperatures ranging

from 0°C to 50°C.

The product when applied to blond hair dyes it an intense black under the conditions described in Example 1.

Examples 3 and 4

5 Example 2 was repeated except that the CARBOPOL 940 thickener at a concentration of 1.0% by weight was replaced firstly with CARBOPOL 941 at a concentration of 0.9% by weight and secondly by polyethyleneglycol 6000 distearate at a concentration of 2.0% by weight.

10 Both of these modified one-pack products stored well without appreciable loss of viscosity under the conditions used in Example 2, and they both successfully dyed blond hair an intense black under similar conditions of use.

Examples 5 and 6

15 Example 2 was repeated except that sodium metabisulphite was replaced either with sodium dithionite (0.5% by weight) or with ascorbic acid (0.5% by weight).

In both cases, hair was dyed black under similar conditions of use.

20 Experiments

The following experiments illustrate the importance of the defined molar ratios of the dye precursors, the pH of the composition and the duration of contact with hair during the dyeing process.

25 Experiment A

30 The procedure described in Example 2 was repeated except that the concentration of MPPD was 1.9% by weight (0.76M), and that of DAP was 0.49% by weight (0.025M). The molar ratio of MPPD to DAP in the composition was accordingly approximately 30:1 which was well outside the upper limit defined by the invention of 10:1.

Blond hair dyed using this composition yielded a brown colour.

Experiment B

35 The procedure described in Example 2 was also repeated except that the concentration of MPPD was 0.5% by weight

(0.02M), and that of DAP was 7.8% by weight (0.4M). The molar ratio of MPPD to DAP in the composition was accordingly 1:20 which was also well outside the lower limit defined by the invention of 1:10.

- 5 Blond hair dyed using this composition was initially dark brown, but after a few days, the hair acquired a distinct redness.

Experiment C

- 10 The procedure described in Example 2 was repeated, except that the composition was adjusted to a pH value of 5, which was below the lower limit defined by the invention of 6.

Blond hair dyed with this composition acquired a brown colour.

15 Experiment D

The procedure described in Example 2 was repeated, except that the composition was used to treat a switch of blond hair for only five minutes which was less than the minimum recommended time of 10 minutes.

- 20 The switch of hair acquired a brown colour.

- It was noted from these experiments that in each case a black colour was not obtained. This illustrates the importance of employing appropriate concentrations of dye precursors, pH of composition and duration of contact time
25 as defined herein.

CLAIMS:

1. A composition for use in the dyeing of keratinous fibres to produce a black colour, which comprises an aqueous, substantially oxygen-free solution of the dye precursors 2-methoxy-p-phenylenediamine and 2,4-diaminophenol, the composition having a pH value of from 6 to 12.
2. A composition according to claim 1, in which the dye precursors together form from 0.25 to 15% by weight of the composition, the molar ratio of one dye precursor to the other being from 1:10 to 10:1.
3. A composition according to claim 1 or 2, in which the dye precursors together form from 1 to 10% by weight of the composition.
4. A composition according to claim 1, 2 or 3, in which the molar ratio of 2-methoxy-p-phenylenediamine to 2,4-diaminophenol in the composition is from 1:5 to 3:1.
5. A composition according to any preceding claim, in which the molar ratio of 2-methoxy-p-phenylenediamine to 2,4-diaminophenol in the composition is from 1:3 to 1:1.
6. A composition according to any preceding claim, in which the dye precursors each form from 0.5 to 10% by weight of the composition.
7. A composition according to any preceding claim, in which the solution is maintained in an oxygen-free condition by the presence of an antioxidant.
8. A composition according to claim 7, in which the antioxidant is ascorbic acid, sodium metabisulphite or

sodium dithionite.

9. A composition according to claim 7 or 8, in which the antioxidant forms from 0.01 to 3% by weight of the composition.

10. A composition according to any preceding claim, which additionally comprises a detergent.

11. A composition according to claim 10, in which the detergent is an anionic detergent chosen from sodium lauryl ether sulphate (2EO) and sodium lauryl ether sulphate (3EO), or a mixture thereof.

12. A composition according to claim 10, in which the detergent is chosen from polyoxyethylene lauryl alcohol (23EO) and oleic diethanolamide, or a mixture thereof.

13. A composition according to any of claims 10 to 12, in which the detergent comprises a mixture of an anionic and a nonionic detergent.

14. A composition according to any of claims 10 to 13, in which the detergent forms from 1 to 15% by weight of the composition.

15. A composition according to any preceding claim, which additionally comprises a thickening agent.

16. A composition according to claim 15, in which the thickening agent is chosen from carboxyvinyl polymers and polyethyleneglycol distearate, or mixtures thereof.

17. A composition according to claim 16, in which the thickener forms from 0.1 to 2% by weight of the composition.

18. A composition according to any preceding claim and substantially as described in any of the Examples.
19. A process for the preparation of a composition for use in the dyeing of keratinous fibres according to any of claims 1 to 18 which comprises
- (i) dissolving in oxygen-free water and dye precursors 2-methoxy-p-phenylene diamine and 2,4-diaminophenol, the composition having a pH of from 6 to 12; and
 - (ii) packaging the composition in a closed container in the substantial absence of oxygen.
20. A closed container, dispenser or applicator containing the composition according to any of claims 1 to 18.
21. A dispenser according to claim 20 which is an aerosol pressurised pack dispenser containing an inert propellant.
22. A method of dyeing keratinous fibres a black colour, which comprises applying to keratinous fibres in the absence of hydrogen peroxide, a composition according to any of claims 1 to 18.



European Patent
Office

EUROPEAN SEARCH REP RT

0074243

Application number

EP 82 30 4596

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. 7)
X,Y	CH-A- 445 722 (WELLA) *The whole document, in particular column 3; example 1*	1-22	A 61 K 7/13
X,Y	FR-A-1 337 012 (SCHWARZKOPF) *Page 2, column 1, line 7 - column 2; abstract 3* & GB - A - 986 020	1-22	
X,Y	FR-A-1 372 525 (INTERPAL) *The whole document, in particular page 3; example 5* & GB - A - 983 207	1-22	
Y	FR-A-2 258 167 (UNILEVER) *Page 9, line 1 - page 10, line 5* & GB - A - 1 489 344	7-21	
A	DE-A-1 492 256 (INTERPAL) *Claims 1,2*		TECHNICAL FIELDS SEARCHED (Int. Cl. 7) A 61 K 7/00
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 05-10-1982	Examiner BENZ K.F.
CATEGORY OF CITED DOCUMENTS			
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	